Response Properties of Periodic Materials Subjected to External Electric and Magnetic Fields

Response properties of periodic materials subjected to external electric and magnetic fields.

Bernard Kirtman, Lorenzo Maschio, Michel Rérat, Michael Springborg

Abstract The ab initio treatment of external field response in crystalline solids poses particular challenges, since the operator representing the external field must be reformulated so to be consistent with periodic boundary conditions. In this chapter, we review our recent work to formulate implementable working equations for polarizability and hyperpolarizabilities in solids, in the framework of a local (gaussian) basis set. This includes the combination of electric field response with geometrical distorsion, i.e. infrared and Raman intensities, as well as piezoelectricity. In addition, we outline a pathway for including magnetic fields in a consistent way, and speculate on future possible developments.

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1 Introduction

The polarization of molecular electrons in an external electric field and the magnetization due to orbital motion in a magnetic field give rise to a large variety of physical properties that are of high interest in science and engineering. Apart from the usual spectroscopic observables, electric and magnetic fields can significantly affect chemical, mechanical and structural properties as well. For ordinary molecules the required quantum theoretical treatment and ab initio computational methods to determine these quantities are at a relatively advanced stage of development. The situation is different, however, for materials that are modeled as being infinite and periodic in 1, 2 or 3 dimensions. That is primarily because the interaction term in the Hamiltonian appropriate for ordinary molecules, is either non-periodic [6] or is periodic only for certain values of the (magnetic) field [7]. Although this difficulty was initially considered over 50 years ago, not until much more recently have suitable solutions been developed (see Refs. [29, 54, 55, 10, 2, 63, 40, 30, 4, 58]).

Despite the fact that there are unique aspects for infinite periodic systems, our general approach has been to exploit the methods that have been successfully developed in molecular quantum chemistry as much as possible. Consistent with that perspective, the implementation of computational methods has been carried out within the CRYSTAL code [14, 12, 9], which utilizes Gaussian-type orbitals (GTOs). This code has the advantage that electron exchange interactions are treated accurately and straightforwardly. It also takes maximum advantage of symmetry, and can run in parallel with a large number of cores (easily up to 4096) for large systems using a basis set containing more than 10^5 functions. There are, of course, other periodic codes - mostly based on plane waves - that also treat some of the properties considered in this chapter.

Even though substantial progress has been made, the treatment of infinite periodic systems is far less advanced than what has been achieved for ordinary molecules. Thus, we shall indicate in our presentation some of the next steps that are on the drawing board and some that may be envisioned in the longer term. Our emphasis will be on the theoretical development although initial applications are included in the references cited.

In the next section (Sec. 2) we specify the translationally invariant one-electron operators that describe the interaction of static or dynamic electric and magnetic fields with periodic systems. Moreover, the important properties of these operators, with regard to their action on periodic orbitals, are discussed. This includes their hermitian character as well as the effect on the orbital phases which, surprisingly can be related to changes in the electric polarization of the material when boundary surfaces are introduced. The Hartree-Fock and Kohn-Sham (HF/KS) perturbation theory treatments of linear and nonlinear optical properties are presented in Sec. 3 and 4. This approach provides a model pathway for ultimately including magnetic properties and properties determined by the simultaneous action of electric and magnetic fields in the future. Electronic spectra are also treated in Sec. 4 through the frequency-dependent linear polarizability.

The next set of properties to be considered, in Sec. 5, concerns the effect of geomet-

rical distortions on the electronic polarization or vice versa. This category includes, for instance, infra-red and Raman intensities, which are determined by internal unit cell deformations. Another example is the direct and converse piezoelectricity associated with (external) strain.
Finally, there is a concluding section that summarizes the current and near term developments that have been discussed in this chapter. We also speculate there about some of the advances, both theoretical and computational, that the longer term future may bring.

Let us briefly introduce the notation, adopted in the following:

- Greek indices $\mu, \nu, \ldots$ will label AO basis functions in the unit cell.
- Direct space lattice vectors will be indicated as **g**,**h**,**n**...
- Latin letters i,j,... will indicate occupied molecular or crystalline orbitals; a,b,... will indicate virtual orbitals; other latin letters like p,q,r,s,... will indicate a general orbital (either occupied or virtual).
- k-vectors of the Brillouin Zone (BZ) sampling in reciprocal space will be indicated as **k**
- A general cartesian direction (x,y,z) will be expressed by lower case letters t, u, v, ...
- Matrices denoted as $S(\mathbf{g}), F(\mathbf{g}), D(\mathbf{g}), \ldots$ represent direct space quantities, while reciprocal space quantities are denoted as $S(\mathbf{k}), F(\mathbf{k}), D(\mathbf{k}), \ldots$.
- Direct space and reciprocal space quantities are connected through standard Fourier and back-Fourier transforms, $\mathscr{F}$ and $\overline{\mathscr{F}}$ respectively:

$$S(\mathbf{k}) = \mathscr{F}\left[S(\mathbf{g})\right]$$
$$S(\mathbf{g}) = \overline{\mathscr{F}}\left[S(\mathbf{k})\right]$$

Atomic units will be also used all along the text, so that we set the absolute value of the electronic charge and its mass, $|e|$ and m, as well as $4\pi\varepsilon_0$, and $\hbar$ all equal to 1.

2 Translationally invariant one-electron operators for external fields

2.1 Basics

In order to appreciate the challenges connected with the theoretical treatment of an infinite, periodic system exposed to electromagnetic fields, it may be useful to start with static fields (thus avoiding time dependence) for a large, finite system (thus avoiding periodic boundary conditions) that is assumed to be neutral (thus avoiding complications due to origin dependence of the dipole moment) and focus on the exact solutions to the Hartree-Fock or Kohn-Sham equations (thus avoiding complications due to a finite basis set). In that case, the complete non-relativistic electronic Hamilton operator is hermitian and equal to

$$\begin{aligned}\hat{H}_e = &\sum_{\nu=1}^{N_e} \hat{h}_{\mathrm{n}}(\mathbf{r}_\nu) + \frac{1}{2} \sum_{\nu_1 \neq \nu_2 = 1}^{N_e} \hat{h}_2(\mathbf{r}_{\nu_1}, \mathbf{r}_{\nu_2}) + \sum_{\nu=1}^{N_e} \hat{h}_{\mathrm{C+xc}}(\mathbf{r}_\nu) \\ &+ \sum_{\nu=1}^{N_e} \hat{h}_{\mathrm{el}}(\mathbf{r}_\nu) + \sum_{\nu=1}^{N_e} \hat{h}_{\mathrm{k+m}}(\mathbf{r}_\nu), \end{aligned} \tag{1}$$

where $\hat{h}_{\mathrm{n}}(\mathbf{r}_\nu)$ is the potential due to the nuclei, $\hat{h}_2(\mathbf{r}_{\nu_1}, \mathbf{r}_{\nu_2})$ describes the electron-electron interactions, $\hat{h}_{\mathrm{C+xc}}(\mathbf{r}_\nu)$ is the Coulomb and exchange-correlation potential, and N_e is the number of electrons. Within the Hartree-Fock approximation, $\hat{h}_{\mathrm{C+xc}}$ is set equal to 0, whereas $\hat{h}_2 = 0$ when using a pure Kohn-Sham density-functional approach. Various hybrid approaches may also be written in the form of Eq. (1) by combining the 2nd and 3rd term on the rhs appropriately.

However, our focus here is on the last two terms. In the next-to-last term we use the scalar potential to take the presence of the electrostatic field into account. Then, assuming that the field $\mathscr{E}$ is position independent

$$\hat{h}_{\mathrm{el}}(\mathbf{r}) = \mathscr{E} \cdot \mathbf{r}. \tag{2}$$

Any dependence of this term on the origin is compensated by a similar dependence in the equivalent nuclear term (not shown). Finally, the operator for the kinetic energy plus magnetic terms is

$$\hat{h}_{\mathrm{k+m}}(\mathbf{r}) = \frac{1}{2} \left[-\imath\nabla + \frac{1}{2c} \mathscr{B} \times (\mathbf{r} - \mathbf{R}_G) \right]^2. \tag{3}$$

where $\mathscr{B}$ is the uniform external magnetic field determined by the vector potential with a gauge origin at $\mathbf{R}_G$. $\mathbf{R}_G$ is unphysical and, in the ideal case that the electronic orbitals are determined exactly, the results will not depend on its choice.

It is well-known that when approximating the exact N_e-electron wavefunction through a single Slater determinant Ψ, the requirement that the expectation value

$\langle\Psi|\hat{H}_e|\Psi\rangle$ is minimal under the constraint that the orbitals are orthonormal, $\langle\psi_{j_1}|\psi_{j_2}\rangle = \delta_{j_1,j_2}$, can be cast into a single-particle Hartree-Fock or Kohn-Sham equations

$$\hat{h}\psi_j(\mathbf{r}) = \sum_{j'} \lambda_{j,j'}\psi_{j'}(\mathbf{r}). \tag{4}$$

The Fock or Kohn-Sham operator $\hat{h}$ is hermitian and the Lagrange multipliers λ may be chosen so that $\lambda_{j,j'} = \varepsilon_j\delta_{j,j'}$ (the canonical choice). Then, a unitary transformation amongst the occupied orbitals will leave the calculated value of any observable unchanged. The reason we mention these well-known facts will become clear below.

For the infinite, periodic system in the absence of any electrostatic or magnetostatic field, the orbitals may be written as Bloch functions,

$$\psi_j(\mathbf{k},\mathbf{r}) = e^{\imath\mathbf{k}\cdot\mathbf{r}}u_j(\mathbf{k},\mathbf{r}) \tag{5}$$

with $u_j(\mathbf{k},\mathbf{r})$ being lattice-periodic. Moreover, the electronic Hamilton operator for the energy per repeated unit will be identical to that of Eq. (1) divided by the number of units N_u and evaluated in the limit $N_u \to \infty$. The number of electrons $N_e = N_u \cdot n_e$ with n_e equal to the number of electrons per repeated unit.

In this case, $\mathbf{k}$ is a good quantum number, and one may calculate the orbitals for each $\mathbf{k}$ separately. Again, a unitary transformation (e.g., for each $\mathbf{k}$ separately) will leave observables unchanged.

However, the interaction with an electrostatic field as represented by Eq. (2) destroys translational invariance. Instead, one may use [44, 8, 45, 30, 23, 32, 4, 46]

$$\mathscr{E}\cdot\mathbf{r} \to \mathscr{E}\cdot\imath e^{\imath\mathbf{k}\cdot\mathbf{r}}\nabla_k e^{-\imath\mathbf{k}\cdot\mathbf{r}} \equiv \hat{h}_{\mathrm{el}}(\mathbf{k},\mathbf{r}), \tag{6}$$

a suggestion that goes back to the work of Blount more than 50 years ago [6]. It is easily verified that $\hat{h}_{\mathrm{el}}(\mathbf{k},\mathbf{r})$ in Eq. (6) preserves translational symmetry. Blount's operator acts on $\mathbf{k}$. Thus, a $\mathbf{k}$-dependent unitary transformation of the occupied orbitals, may lead to a change in the energy. Actually, even the very simple unitary transformation whereby the individual occupied are modified by $\mathbf{k}$ dependent phase factors can lead to such an effect. In fact, by making a 'pathological' choice of the phase factors it is possible to change the energy due to the electrostatic field essentially arbitrarily, which implies that there is no lowest energy and that the variational principle will fail. The solution to this dilemma is that the phase factors or, in general, the unitary transformation cannot be chosen randomly. Different choices correspond to modeling large, finite samples of the same material but with different shapes and/or surface charges [59, 60].

A second complication is that $\hat{h}_{\mathrm{el}}(\mathbf{k},\mathbf{r})$ is hermitian only for functions whose overlap is $\mathbf{k}$ independent, i.e., functions $\{f_n\}$ obeying $\nabla_k\langle f_p|f_q\rangle = \mathbf{0}$. This is the case for (orthonormal) electronic orbitals but not in the general case. Moreover, for static magnetic fields the corresponding condition, as shown later, is much more difficult to satisfy. Thus, we proceed here with a more general solution, which is to make the replacement

$$\hat{h}_{\rm el}(\mathbf{k},\mathbf{r}) \rightarrow \frac{1}{2}\left[\hat{h}_{\rm el}(\mathbf{k},\mathbf{r}) + \hat{h}^{\dagger}_{\rm el}(\mathbf{k},\mathbf{r})\right]. \tag{7}$$

If one derives the Fock or Kohn-Sham equations in the usual manner [see below Eq. (3)], then this substitution turns out to yield exactly the same **k**-dependent single-particle operator that was given in Eq. (6). Nonetheless, for the reasons mentioned above, one must still subsequently specify some criterion for how to choose the orbital phase factors in order to find a unique solution of even the canonical form of the single-particle equation,

$$\hat{h}(\mathbf{k})\psi_j(\mathbf{k},\mathbf{r}) = \varepsilon_j(\mathbf{k})\psi(\mathbf{k},\mathbf{r}) \tag{8}$$

The story is different, however, when a magnetostatic field is included. In that event it may be suggested to make a substitution like that of Eq. (6) in the expression of Eq. (3). Actually, the magnetic field term in Eq. (3) is derived from the vector potential $\mathbf{A} = \mathbf{A}_0 e^{\imath\mathbf{q}\cdot(r-R_G)}$ where the wave vector $\mathbf{q}$ for a constant field goes to zero and the magnetic field is given by $\mathscr{B} = \nabla\times\mathbf{A}$. The substitution of Eq. (6) can, then, be viewed as replacing $\mathscr{E}\cdot\mathbf{r}$ by $\mathscr{E}\cdot\hat{\Omega}(\mathbf{k}) = \mathscr{E}\cdot\imath e^{\imath\mathbf{k}\cdot\mathbf{r}}\nabla_k e^{-\imath\mathbf{k}\cdot\mathbf{r}} = \mathscr{E}\cdot(\mathbf{r}+\imath\nabla_k)$ [52]. Thus, one might consider replacing the linear magnetic field term in the kinetic-energy operator $\frac{1}{2}\left(\hat{\mathbf{p}}+\frac{1}{c}\mathbf{A}\right)^2$ operator by an expression that involves the angular momentum operator $\mathscr{B}\cdot\hat{L} = \frac{1}{c}\mathscr{B}\cdot(-\imath\hat{\Omega}(\mathbf{k})\times\nabla)$. However, the resulting operator is hermitian only for special circumstances, i.e., for functions $\{f_n\}$ for which $\nabla_k\cdot\langle f_p|\hat{p}|f_q\rangle = 0$ that in most instances are irrelevant.
Hermiticity can be restored following an approach similar to that of Eq. (7); in this case there are two different possibilities for the single-particle operator that come readily to mind:

$$\begin{aligned}
&\frac{1}{2m}\left[-\imath\nabla + \frac{1}{2c}\mathscr{B}\times(\mathbf{r}-\mathbf{R}_G)\right]^2 \\
&\rightarrow \frac{1}{2m}\left(-\imath\nabla + \frac{1}{2c}\mathscr{B}\times\imath e^{\imath\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}_G)}\nabla_k e^{-\imath\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}_G)}\right)^{\dagger} \\
&\quad\cdot\left(-\imath\nabla + \frac{1}{2c}\mathscr{B}\times\imath e^{\imath\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}_G)}\nabla_k e^{-\imath\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}_G)}\right)
\end{aligned} \tag{9}$$

or

$$\begin{aligned}
&\frac{1}{2m}\left[\imath\nabla - \frac{1}{2c}\mathscr{B}\times(\mathbf{r}-\mathbf{R}_G)\right]^2 \\
&\rightarrow \frac{1}{4m}\left[\left(-\imath\nabla + \frac{1}{2c}\mathscr{B}\times\imath e^{\imath\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}_G)}\nabla_k e^{-\imath\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}_G)}\right)^{\dagger}\right]^2 \\
&\quad+\frac{1}{4m}\left[-\imath\nabla + \frac{1}{2c}\mathscr{B}\times\imath e^{\imath\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}_G)}\nabla_k e^{-\imath\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}_G)}\right]^2 \\
&\equiv \frac{1}{2}\left[\hat{h}_{\rm km,1}(\mathbf{k},\mathbf{r}) + \hat{h}_{\rm km,2}(\mathbf{k},\mathbf{r})\right].
\end{aligned} \tag{10}$$

It can be shown [60] that the two expressions lead to the same expectation value for the energy due to the magnetic field. Both operators in Eqs. (9) and (10) act, again, on the **k**-dependence of the orbitals. In this case it can be demonstrated that the effect of **k**-dependent orbital phase factors and/or **k**-dependent unitary transformations among the occupied orbitals is mathematically equivalent to introducing a different magnetic field gauge origin for different orbitals.Since the gauge origins are unphysical, however, they cannot alter the magnetic energy, at least in the case that the single-particle orbitals are calculated exactly.
Again, we may derive single-particle equations by requiring that the total energy is at a minimum together with the condition that the orbitals are orthonormal. It turns out that the Fock or Kohn-Sham operator then involves either $\hat{h}_{\mathrm{km},1}(\mathbf{k},\mathbf{r})$ or $\hat{h}_{\mathrm{km},2}(\mathbf{k},\mathbf{r})$, but not both, so that it is, in general, non-hermitian. However, one can show that it is hermitian for the exact eigenfunctions.

2.2 LCAO-CO Formulation

The next step is to formulate the Fock or Kohn-Sham equation within the LCAO-CO approximation. In the following we will focus on the electric field perturbation, not the least because the magnetic field case has yet to be developed. As seen above, in either case our approach relies on a formulation of the electronic operator for interaction with the field which, in the Bloch basis, is diagonal with respect to the reciprocal space **k** vector. Provided the system has a non-zero bandgap, this operator may be written for the electric field operator as [see Eq. (6)]:

$$\mathscr{E}\cdot\hat{\Omega}(\mathbf{k}) = \mathscr{E}\cdot\imath e^{\imath\mathbf{k}\cdot\mathbf{r}}\nabla_k e^{-\imath\mathbf{k}\cdot\mathbf{r}} = \sum_{t=x,y,z}\mathscr{E}_t\,\hat{\Omega}_t(\mathbf{k}) \quad . \tag{11}$$

The evaluation of $\hat{\Omega}$ requires a derivative with respect to **k**. Algorithms capable of dealing with this derivative have been implemented in plane wave codes [22, 16, 2, 15] although the role of crystal orbital phase factors is often ignored, as discussed in this chapter and in Refs. [4] and [35]. A rather different approach, appropriate for an atomic orbital (AO) basis, is employed herein.
The effect of the electric field interaction term in (11) can be treated by finite field methods or by perturbation theory. Here we focus on the latter approach.
The first-order perturbation energy, which is equal to the mean value of Ω_k determines the dipole moment. This property is ill-defined in infinite periodic systems. For instance, the polymer ...ABAB... is equivalent to ...BABA... and, in that case, the dipole moment could be either positive or negative. Mathematically, the ambiguity is associated with the phases of the Bloch orbitals [4, 29]. Physically, the possible values can be related to surface charges and/or shape of the large finite system that is being modeled [61, 59], even though the corresponding infinite periodic system does not have any surfaces. For the special case of 1D periodic systems, the dipole

moment is limited to values that differ from each other by an integer multiple of the cell parameter [4, 31] Although there is an ambiguity in the value of the dipole moment, that is not the case for derivatives of the dipole moment with respect to the field(s), i.e. for (hyper)polarizabilities. This has previously been demonstrated for 1D periodic systems [4] and we will see in the next section that it can be generalized for 3D systems as well. We shall need the effect of the operator $\hat{\Omega}(\mathbf{k})$ on an arbitrary field-dependent crystal orbital (CO) expanded in an atomic orbital (AO) basis $\mid \phi_i \rangle = \sum_\nu \mid \nu \rangle C_{\nu,i}$. Projecting on the left hand side with the AO basis function $\langle \mu \mid$ yields the mixed AO/CO relation [45]

$$\begin{aligned} &\sum_\nu \langle \mu \mid \hat{\Omega}_t(\mathbf{k}) \mid \nu \rangle C_{\nu,i}(\mathbf{k}) \\ &\quad = \sum_\nu \left[(Z_t)_{\mu\nu}(\mathbf{k}) + \imath S^{(k_t)}_{\mu\nu}(\mathbf{k}) + \imath S_{\mu\nu}(\mathbf{k}) \frac{\partial}{\partial k_t} \right] C_{\nu,i}(\mathbf{k}) \end{aligned} \tag{12}$$

Here $Z_t(\mathbf{k})$ is the AO matrix that represents the component of the electronic position coordinate along t and $S^{(k_t)}(\mathbf{k})$ is the derivative of the AO overlap matrix, S, with respect to the wave vector k_t. This last relation is valid at any arbitrary field and geometry.

3 Coupled Perturbed Hartree-Fock (CPHF) and Kohn-Sham (CPKS) Static (Hyper)polarizabilities

In the previous section we have developed the proper form of the electric field interaction term to be included in the Hamiltonian for a periodic system. The wavefunction and electric dipole properties can then be obtained, for example, through a periodic coupled-pertubed Hartree-Fock (CPHF) or Kohn-Sham (CPKS) approach. Such a CPHF/CPKS treatment has been developed [18] and implemented [19, 20], by some of the present authors, in the CRYSTAL program, that uses a local Gaussian basis set [13, 11]. In this section we will further develop the formalism, present operative equations as they have been implemented, and focus on the role of the ∇_k operator in the electric field terms.

3.1 CPHF treatment

We write the reciprocal space eigenvectors of the Fock matrix as a function of electric field using a Taylor series in the field components:

$$C(\mathbf{k}) = C^{(0)}(\mathbf{k}) + \sum_{t=x,y,z} \mathscr{E}_t C^{(\mathscr{E}_t)}(\mathbf{k}) + \sum_{t,u=x,y,z} \mathscr{E}_t \mathscr{E}_u C^{(\mathscr{E}_t,\mathscr{E}_u)}(\mathbf{k}) + \ldots \tag{13}$$

Then the perturbed first-order k-space density matrix $D(\mathbf{k})$ may be obtained as:

$$D^{(\mathscr{E}_t)}(\mathbf{k}) = C^{(\mathscr{E}_t)}(\mathbf{k})\, n C^{(0)\dagger}(\mathbf{k}) + C^{(0)}(\mathbf{k})\, n C^{(\mathscr{E}_t)\dagger}(\mathbf{k}) \tag{14}$$

where n is the diagonal occupancy matrix and we will, henceforth, assume closed shells so that the diagonal elements equal 0 or 2. Similarly, the second-order expression for $D^{(\mathscr{E}_t,\mathscr{E}_u)}(\mathbf{k})$ is given by:

$$\begin{aligned} D^{(\mathscr{E}_t,\mathscr{E}_u)}(\mathbf{k}) = {} & C^{(\mathscr{E}_t,\mathscr{E}_u)}(\mathbf{k})\, n C^{(0)\dagger}(\mathbf{k}) + C^{(\mathscr{E}_u)}(\mathbf{k})\, n C^{(\mathscr{E}_t)\dagger}(\mathbf{k}) \\ & + C^{(\mathscr{E}_t)}(\mathbf{k})\, n C^{(\mathscr{E}_u)\dagger}(\mathbf{k}) + C^{(0)}(\mathbf{k})\, n C^{(\mathscr{E}_t,\mathscr{E}_u)\dagger}(\mathbf{k}) \end{aligned} \tag{15}$$

It is common to express the perturbed coefficient vectors as a linear combination of the unperturbed vectors, i.e.

$$\frac{\partial}{\partial \mathscr{E}_t} C(\mathbf{k}) = C^{(\mathscr{E}_t)}(\mathbf{k}) = C^{(0)}(\mathbf{k})\, U^{(\mathscr{E}_t)}(\mathbf{k}) \tag{16}$$

$$\frac{\partial^2}{\partial \mathscr{E}_t \partial \mathscr{E}_u} C(\mathbf{k}) = C^{(\mathscr{E}_t,\mathscr{E}_u)}(\mathbf{k}) = C^{(0)}(\mathbf{k})\, U^{(\mathscr{E}_t,\mathscr{E}_u)}(\mathbf{k}) \tag{17}$$

where the U matrices are calculated self-consistently by solving the first- and second- order non-canonical CPHF(KS) equations [25, 18]:

$$U_{ij}^{(\mathscr{E}_t)}(\mathbf{k}) = 0 \tag{18}$$

$$U_{ab}^{(\mathscr{E}_t)}(\mathbf{k}) = 0 \tag{19}$$

$$U_{ia}^{(\mathscr{E}_t)}(\mathbf{k}) = \frac{G_{ia}^{(\mathscr{E}_t)}(\mathbf{k})}{\varepsilon_a^{(0)}(\mathbf{k}) - \varepsilon_i^{(0)}(\mathbf{k})} \tag{20}$$

$$U_{ij}^{(\mathscr{E}_t,\mathscr{E}_u)}(\mathbf{k}) = -1/2 P_{t,u} \sum_a U_{ai}^{(\mathscr{E}_t)*}(\mathbf{k})\, U_{aj}^{(\mathscr{E}_u)}(\mathbf{k}) \tag{21}$$

$$U_{ab}^{(\mathscr{E}_t,\mathscr{E}_u)}(\mathbf{k}) = -1/2 P_{t,u} \sum_i U_{ia}^{(\mathscr{E}_t)*}(\mathbf{k})\, U_{ib}^{(\mathscr{E}_u)}(\mathbf{k}) \tag{22}$$

$$\begin{aligned} U_{ia}^{(\mathscr{E}_t,\mathscr{E}_u)}(\mathbf{k}) = \Bigg\{ P_{t,u} \Bigg(\sum_j G_{ij}^{(\mathscr{E}_t)}(\mathbf{k})\, U_{ja}^{(\mathscr{E}_u)}(\mathbf{k}) - \sum_b U_{ib}^{(\mathscr{E}_t)}(\mathbf{k}) G_{ba}^{(\mathscr{E}_u)}(\mathbf{k}) + \imath \frac{\partial U_{ia}^{(\mathscr{E}_t)}(\mathbf{k})}{\partial k_u} \Bigg) \\ + G_{ia}^{(\mathscr{E}_t,\mathscr{E}_u)}(\mathbf{k}) \Bigg\} \left[\varepsilon_a^{(0)}(\mathbf{k}) - \varepsilon_i^{(0)}(\mathbf{k}) \right]^{-1} \end{aligned} \tag{23}$$

Here $P_{t,u}$ represents a sum over the permutation of $\mathscr{E}_t$ and $\mathscr{E}_u$; also although not explicitly indicated, the unperturbed orbital energies $\varepsilon_i^{(0)}$ and $\varepsilon_a^{(0)}$ depend on $\mathbf{k}$ (for a 0D system $\mathbf{k} = \mathbf{0}$). The matrix element $G_{ia}^{(\mathscr{E}_t)}(\mathbf{k})$, for example, is obtained from the partial derivatives of the AO Fock matrix with respect to the field, that is subsequently transformed to the CO basis with i an occupied and a an unoccupied orbital ($\sum_{\mu\nu} C_{\mu i}^{(0)*}(\mathbf{k}) \frac{\partial F_{\mu\nu}(\mathbf{k})}{\partial \mathscr{E}_t} C_{\nu a}^{(0)}(\mathbf{k})$). This matrix element contains the bielectronic integrals multiplied by the first-order perturbed density matrix $D^{(\mathscr{E}_t)}(\mathbf{k})$ and thereby depends upon $U^{(\mathscr{E}_t)}(\mathbf{k})$. It also contains the explicit first-order electric field term of the Hamiltonian [see definition in Eq. (12)] which, in the CO basis, is:

$$\begin{aligned} \Omega_t(\mathbf{k}) &= C^{(0)\dagger}(\mathbf{k}) \left(Z_t(\mathbf{k}) + \imath S^{(k_t)}(\mathbf{k}) + \imath \left[S(\mathbf{k}) C^{(0)}(\mathbf{k})\, Q_t(\mathbf{k}) C^{(0)\dagger}(\mathbf{k}) S(\mathbf{k}) \right] \right) C^{(0)}(\mathbf{k}) \\ &= C^{(0)\dagger}(\mathbf{k}) \left(Z_t(\mathbf{k}) + \imath S^{(k_t)}(\mathbf{k}) \right) C^{(0)}(\mathbf{k}) + \imath Q_t(\mathbf{k}) \end{aligned} \tag{24}$$

The CO matrix $Q_t(\mathbf{k})$ is due to the partial derivative with respect to $\mathbf{k}_t$ in $\hat{\Omega}$ acting on the unperturbed coefficient matrix. It is defined through the relation:

$$\frac{\partial}{\partial k_t} C^{(0)}(\mathbf{k}) = C^{(0)}(\mathbf{k})\, Q_t(\mathbf{k}) \ . \tag{25}$$

and may be calculated as (for $i \neq j$):

$$Q_{ij}^{k_t}(\mathbf{k}) = \frac{G_{ij}^{k_t}(\mathbf{k}) - \varepsilon_j^{(0)}(\mathbf{k}) S_{ij}^{k_t}(\mathbf{k})}{\varepsilon_j^{(0)}(\mathbf{k}) - \varepsilon_i^{(0)}(\mathbf{k})} \tag{26}$$

where $G_{ij}^{k_t}(\mathbf{k})$ and $S_{ij}^{k_t}(\mathbf{k})$ are the derivatives of the Fock and overlap matrices transformed to the CO basis, i.e. $\sum_{\mu\nu} C_{\mu i}^{(0)*(\mathbf{k})} \frac{\partial F_{\mu\nu}(\mathbf{k})}{\partial k_t} C_{\nu j}^{(0)}(\mathbf{k})$ and $\sum_{\mu\nu} C_{\mu i}^{(0)*}(\mathbf{k}) \frac{\partial S_{\mu\nu}(\mathbf{k})}{\partial k_t} C_{\nu j}^{(0)}(\mathbf{k})$,

respectively. The diagonal elements of $Q^{k_t}(\mathbf{k})$ are determined by the normalization condition which leads to $-\frac{1}{2}S^{k_t}_{ii}(\mathbf{k})$ for the real part. However, there is also an undetermined imaginary part (which reflects an arbitrary phase factor for each CO coefficient vector) [4, 31, 26]. This imaginary contributionn leads to the indeterminacy in the dipole moment described earlier. It does not, however, affect the polarizability and hyperpolarizabilities as we will see later.
By applying the perturbation theory discussed above to the periodic Hartree-Fock (see later for Kohn-Sham) equations, where the Hamiltonian contains the electric field perturbation term characterized by Ω_t, as defined in Eq. (24), one obtains the following expressions for the static dipolar electric field properties of closed-shell systems:

1. Dipole Moment

$$\mu_t = -\frac{\partial E^{TOT}}{\partial \mathscr{E}_t} = \frac{2}{n_k}\Re\sum_{\mathbf{k}}^{BZ} Tr\left[\Omega_t(\mathbf{k})\, n\right] \tag{27}$$

   where n is the diagonal electronic occupation matrix.
   Note that the imaginary diagonal elements of the Q matrix contribute to the dipole moment [cf. Eq. (24)]. For real finite systems this contribution will cancel when ignoring structural responses [61].

2. Polarizability

$$\alpha_{tu} = -\frac{\partial^2 E^{TOT}}{\partial \mathscr{E}_t \partial \mathscr{E}_u} = \frac{2}{n_k}\Re\left\{P_{t,u}\sum_{\mathbf{k}}^{BZ} Tr\left[\Omega_t(\mathbf{k})U^{(\mathscr{E}_u)}(\mathbf{k})\, n\right]\right\} \tag{28}$$

   The diagonal blocks of U vanish. Therefore, only the off-diagonal blocks of Ω, and thereby Q, contribute to the polarizability. Thus, there is no indeterminacy in α.
3. First hyperpolarizability

$$\beta_{tuv} = -\frac{\partial^3 E^{TOT}}{\partial \mathscr{E}_t \partial \mathscr{E}_u \partial \mathscr{E}_v} = \frac{2}{n_k}\Re\left\{P_{t,u,v}\sum_{\mathbf{k}}^{BZ} Tr\left[\, n\, U^{(\mathscr{E}_t)\dagger}(\mathbf{k})\left(G^{(\mathscr{E}_u)}(\mathbf{k})U^{(\mathscr{E}_v)}(\mathbf{k}) - U^{(\mathscr{E}_v)}(\mathbf{k})G^{(\mathscr{E}_u)}(\mathbf{k}) + \imath\frac{\partial U^{(\mathscr{E}_v)}(\mathbf{k})}{\partial k_u}\right)\right]\right\} \tag{29}$$

   Now diagonal terms of Q do appear in $G^{(\mathscr{E}_u)}$, and also in $\frac{\partial U^{(\mathscr{E}_v)}}{\partial \mathbf{k}_u}$ even though the diagonal blocks of $U^{(\mathscr{E}_v)}$ itself vanish. The signs are opposite and then β, like α, is completely determined. The 3D expression for $\frac{\partial U^{(\mathscr{E}_v)}}{\partial \mathbf{k}_u}$ and the cancellation of the diagonal terms of Q is exactly analogous to the 1D treatment presented elsewhere (see Refs. [4] and [30]).
4. Second hyperpolarizability

$$\gamma_{tuvw} = -\frac{\partial^4 E^{TOT}}{\partial \mathscr{E}_t \partial \mathscr{E}_u \partial \mathscr{E}_v \partial \mathscr{E}_w} =$$
$$\frac{1}{n_k}\Re\sum_{\mathbf{k}}^{BZ} P_{t,u,v,w} Tr\Big[\, n\, U^{(\mathscr{E}_t)\dagger}(\mathbf{k})\Big(G^{(\mathscr{E}_u)}(\mathbf{k})U^{(\mathscr{E}_v;\mathscr{E}_w)}(\mathbf{k}) - U^{(\mathscr{E}_v;\mathscr{E}_w)}(\mathbf{k})G^{(\mathscr{E}_u)}(\mathbf{k})$$
$$+\ \frac{1}{2}W^{(\mathscr{E}_u;\mathscr{E}_v)}U^{(\mathscr{E}_w)}(\mathbf{k}) - \frac{1}{2}U^{(\mathscr{E}_w)}(\mathbf{k})\varepsilon^{(\mathscr{E}_u;\mathscr{E}_v)}(\mathbf{k})\Big) + \imath n\, U^{(\mathscr{E}_v;\mathscr{E}_w)\dagger}(\mathbf{k})\frac{\partial U^{(\mathscr{E}_t)}(\mathbf{k})}{\partial k_u}\Big] \tag{30}$$

In the previous equation, $W^{(\mathscr{E}_u;\mathscr{E}_v)}$ represents the second derivative of $C^{(0)\dagger}BC^{(0)}$ with respect to the field along $\mathscr{E}_u$ and $\mathscr{E}_v$ where B is the sum of the Coulomb and exchange potentials in the Bloch atomic orbitals basis set.
Under the same conditions as above, it can be shown that γ does not depend on the imaginary diagonal elements of the Q matrix.

3.2 Extension to CPKS

As usual the exchange-correlation (XC) terms require special attention. In that regard we utilize the numerical approach of Pople and co-workers [50]. Thus, the electron density $\rho(r_i)$ and its derivative $\rho^t(r_i)$ with respect to the field $\mathscr{E}_t$ are expressed at each point r_i of a grid as follows:

$$\rho(r_i) = \sum_{\mu,\nu}\sum_{g} D^{g(0)}_{\mu\nu}\chi^0_\mu(r_i)\chi^g_\nu(r_i) \tag{31}$$

$$\rho^t(r_i) = \sum_{\mu,\nu}\sum_{g} D^{g(\mathscr{E}_t)}_{\mu\nu}\chi^0_\mu(r_i)\chi^g_\nu(r_i) \tag{32}$$

which leads to the gradients:

$$\nabla\rho(r_i) = \sum_{\mu,\nu}\sum_{g} D^{g(0)}_{\mu\nu}\nabla(\chi^0_\mu(r)\chi^g_\nu(r))_{r_i} \tag{33}$$

$$\nabla\rho^t(r_i) = \sum_{\mu,\nu}\sum_{g} D^{g(\mathscr{E}_t)}_{\mu\nu}\nabla(\chi^0_\mu(r)\chi^g_\nu(r))_{r_i} \tag{34}$$

$D^{g(0)}_{\mu\nu}$ and $D^{g(\mathscr{E}_t)}_{\mu\nu}$ are the zeroth- and first-order perturbed density matrix elements between μ and ν atomic orbitals belonging to the origin and g cells, respectively, in the direct space.
If f^{XC} denotes an exchange-correlation, then the XC part of the Fock-matrix is

$$F^{XC}_{DFT} = \sum_i w_i\left[\frac{\partial f^{XC}}{\partial\rho}\chi^0_\mu\chi^g_\nu + 2\frac{\partial f^{XC}}{\partial|\nabla\rho|^2}\nabla\rho\cdot\nabla(\chi^0_\mu\chi^g_\nu)\right]_{r_i} \tag{35}$$

with the geometrical weights w_i determined according to an atomic partition, which is field-independent. Since the atomic orbitals are also field-independent the field derivatives of F_{DFT}^{XC}, which are needed to obtain the first-order perturbed orbitals, as described in the previous sub-section, are given by:

$$\begin{aligned} F_{DFT}^{XC(\mathscr{E}_t)} = \sum_i w_i \Bigg\{ & \left[\frac{\partial^2 f^{XC}}{\partial \rho^2} \rho^t + 2 \frac{\partial^2 f^{XC}}{\partial \rho \partial \mid \nabla \rho \mid^2} \nabla \rho \cdot \nabla \rho^t \right] \chi_\mu^0 \chi_\nu^g \\ & + 2 \left[\frac{\partial^2 f^{XC}}{\partial \rho \partial \mid \nabla \rho \mid^2} \rho^t + 2 \frac{\partial^2 f^{XC}}{(\partial \mid \nabla \rho \mid^2)^2} \nabla \rho \cdot \nabla \rho^t \right] \nabla \rho \cdot \nabla (\chi_\mu^0 \chi_\nu^g) \\ & + 2 \frac{\partial f^{XC}}{\partial \mid \nabla \rho \mid^2} \nabla \rho^t \cdot \nabla (\chi_\mu^0 \chi_\nu^g) \Bigg\}_{r_i} \end{aligned} \tag{36}$$

where the field derivatives are taken from Eqs. (31)–(34). In the expression Eq. (35), we have assumed that the exchange-correlation depends only on ρ and $|\nabla\rho|^2$, but it can be easily generalized to include more complicated functionals. In addition, there is a direct contribution to the static β, for example, due to the third derivative of f^{XC} with respect to the fields [42]:

$$\begin{aligned} \beta_{tuv}^{DFT} = \sum_i w_i P_{t,u,v} \Bigg[& \frac{\partial^3 f^{XC}}{\partial \rho^3} \rho^t \rho^u \rho^v + 2 \frac{\partial^3 f^{XC}}{\partial \rho^2 \partial \mid \nabla \rho \mid^2} \left(\rho^t \rho^u \nabla \rho \cdot \nabla \rho^v \right) \\ & + 4 \frac{\partial^3 f^{XC}}{\partial \rho \partial (\mid \nabla \rho \mid^2)^2} \left(\rho^t \nabla \rho \cdot \nabla \rho^u \nabla \rho \cdot \nabla \rho^v \right) \\ & + 8 \frac{\partial^3 f^{XC}}{\partial (\mid \nabla \rho \mid^2)^3} \nabla \rho \cdot \nabla \rho^t \nabla \rho \cdot \nabla \rho^u \nabla \rho \cdot \nabla \rho^v + 2 \frac{\partial^2 f^{XC}}{\partial \rho \partial \mid \nabla \rho \mid^2} \left(\rho^t \nabla \rho^u \cdot \nabla \rho^v \right) \\ & + 4 \frac{\partial^2 f^{XC}}{(\partial (\mid \nabla \rho \mid^2)^2} \left(\nabla \rho \cdot \nabla \rho^t \nabla \rho^u \cdot \nabla \rho^v \right) \Bigg]_{\mathbf{r_i}} \end{aligned} \tag{37}$$

A similar, but considerably more complicated, expression using also the second derivatives $\rho^{tu}(r_i)$ and $\nabla\rho^{tu}(r_i)$ with respect to $\mathscr{E}_t$ and $\mathscr{E}_u$ can be written for the second hyperpolarizability (see Ref. [41]). This expression contains functional fourth derivatives of f^{XC} with respect to ρ and/or its gradient. Fortunately, these derivatives can be obtained automatically (see Ref. [41]). Finally, in the above we have, for convenience, assumed that f^{XC} depends only on ρ and $|\nabla\rho|^2$, although it can be extended to more complicated functionals as well.

4 Linear and Nonlinear Optical Properties

4.1 Dynamic Linear Polarizabilities and Optical Spectra

If the field is frequency (ω)-dependent, time-dependent perturbation theory leads to the two following U matrices (see Refs. [56, 28] for the molecular or $\mathbf{k}=\mathbf{0}$ case, and Refs. [3, 17] for periodic systems):

$$U_{ia}^{(\mathscr{E}_t[\pm\omega])}(\mathbf{k}) = \lim_{\eta\to 0^+} \frac{G_{ia}^{(\mathscr{E}_t[\pm\omega])}(\mathbf{k})}{\varepsilon_a^{(0)}(\mathbf{k}) - \varepsilon_i^{(0)}(\mathbf{k}) \pm \omega + \imath\eta} = -U_{ai}^{(\mathscr{E}_t[\mp\omega])*}(\mathbf{k}) \qquad (38)$$

where $G_{ia}^{(\mathscr{E}_t[\pm\omega])}(\mathbf{k})$ is defined in Sec. 3.1 except that now the electric field in Fock matrix element is ω-frequency dependent. η is a physical damping factor giving the width of the peak due to the inverse lifetime of the excited states (supposed to be the same in the UV-visible range of energy) It is not easy to evaluate the lifetime. Usually the energy resolution of the experimental equipment - typically $\eta \simeq 0.1$eV in UV-visible measurements - is used.
Solution of Eq. (38) for the $U^{(\mathscr{E}_t[\pm\omega])}(\mathbf{k})$ matrices can be obtained by fixing the value of ω and, then, solving iteratively. Near resonances ($\omega \simeq \varepsilon_a^{(0)} - \varepsilon_i^{(0)}$), convergence can be difficult to obtain; in that case a convergence accelerator such as direct inversion in the iterative subspace (DIIS) becomes necessary (see Refs. [51, 21]). Then an optical absorption spectrum can, in principle, be simulated through a scan of ω values in the desired UV-visible frequency range with the relative peak intensity at a given frequency being obtained from the imaginary part of the optical (high-frequency) dielectric matrix ε^∞ for a non-zero value of the damping factor η. At low frequency ($\omega < 1$ eV or $\lambda > 1000$ nm), the vibrational contribution to the polarizability can become large depending upon the magnitude of the Born charges. This contribution will not be considered in the following. Thus, we will assume that the vibrational transition frequencies are negligible compared to ω. The wavelength λ, on the other hand, is assumed to be much larger than the dimensions of the unit cell.
If we replace the static U in Eq. (28) with its frequency-dependent counterpart from Eq. (38), then (after including a simple multiplicative factor to convert from polarizability to dielectric matrix) we find that the imaginary part of ε_{tu}^∞ is:

$$\begin{aligned}\Im(\varepsilon_{tu}^\infty[\omega]) &= \Im\left(\frac{4\pi}{V}\alpha_{t[-\omega]u[+\omega]}\right) \\ &= \frac{8\pi}{V}\frac{1}{n_k}\Im\{P_{t[-\omega],u[+\omega]}\sum_{\mathbf{k}}^{BZ}\sum_{i}^{occ}\sum_{a}^{virt}\Omega_{t,ia}(\mathbf{k})U_{ai}^{(\mathscr{E}_u[+\omega])}(\mathbf{k})\}\end{aligned} \qquad (39)$$

where α and V are the unit cell polarizability and volume, respectively. Note that the dielectric matrix elements are purely real if $\eta = 0$.
In order to exhibit the pole structure of the dielectric matrix we reformulate Eq. (38)

as:

$$U_{ia}^{(\mathscr{E}_t[\pm\omega])}(\mathbf{k}) = \lim_{\eta\to 0^+} \frac{\Omega_{t,ia}(\mathbf{k}) + \sum_{\mathbf{k}'}\sum_j\sum_b \left(U_{jb}^{(\mathscr{E}_t[\pm\omega])}(\mathbf{k}')B_{ia,jb}(\mathbf{k},\mathbf{k}') + U_{jb}^{(\mathscr{E}_t[\mp\omega])*}(\mathbf{k}')B_{ia,bj}(\mathbf{k},\mathbf{k}')\right)}{\varepsilon_a^{(0)}(\mathbf{k}) - \varepsilon_i^{(0)}(\mathbf{k}) \pm \omega + \imath\eta} \tag{40}$$

where $B_{ia,jb}(\mathbf{k},\mathbf{k}')$ and $B_{ia,bj}(\mathbf{k},\mathbf{k}')$ are defined as follows:

$$B_{ia,jb}(\mathbf{k},\mathbf{k}') = [2\langle i_{\mathbf{k}} b_{\mathbf{k}'}|a_{\mathbf{k}} j_{\mathbf{k}'}\rangle - \langle i_{\mathbf{k}} b_{\mathbf{k}'}|j_{\mathbf{k}'} a_{\mathbf{k}}\rangle] \tag{41}$$

$$B_{ia,bj}(\mathbf{k},\mathbf{k}') = [2\langle i_{\mathbf{k}} j_{\mathbf{k}'}|a_{\mathbf{k}} b_{\mathbf{k}'}\rangle - \langle i_{\mathbf{k}} j_{\mathbf{k}'}|b_{\mathbf{k}'} a_{\mathbf{k}}\rangle] \tag{42}$$

The notation $\langle ij|ab\rangle$ is used for the bielectronic integral $\langle i(1)j(2)|\frac{1}{r_{12}}|a(1)b(2)\rangle$. Even if the explicit calculation of such quantities poses practical challenges related to the convergence of the Coulomb Fourier series, we introduce them here since they are useful from a formal point of view to elucidate connections with the TDHF formalism.
We may, then, solve for the converged self-consistent $U(\mathbf{k})$ by re-writing Eq. (40):

$$\begin{aligned} &U_{ia}^{(\mathscr{E}_t[\pm\omega])}(\mathbf{k}) \\ &= \lim_{\eta\to 0^+} \left\{ \frac{\Omega_{t,ia}(\mathbf{k}) + U_{ia}^{(\mathscr{E}_t[\pm\omega])}(\mathbf{k})B_{ia,ia}(\mathbf{k},\mathbf{k}) + U_{ia}^{(\mathscr{E}_t[\mp\omega])*}(\mathbf{k})B_{ia,ai}(\mathbf{k},\mathbf{k})}{\varepsilon_a^{(0)}(\mathbf{k}) - \varepsilon_i^{(0)}(\mathbf{k}) \pm \omega + \imath\eta} \right. \\ &\left. + \frac{\sum_{(\mathbf{k}',j,b)\neq(\mathbf{k},i,a)} \left(U_{jb}^{(\mathscr{E}_t[\pm\omega])}(\mathbf{k}')B_{ia,jb}(\mathbf{k},\mathbf{k}') + U_{jb}^{(\mathscr{E}_t[\mp\omega])*}(\mathbf{k}')B_{ia,bj}(\mathbf{k},\mathbf{k}')\right)}{\varepsilon_a^{(0)}(\mathbf{k}) - \varepsilon_i^{(0)}(\mathbf{k}) \pm \omega + \imath\eta} \right\} \end{aligned} \tag{43}$$

which yields after some manipulation[1]:

$$\begin{aligned} U_{ia}^{(\mathscr{E}_t[\pm\omega])}(\mathbf{k}) = \lim_{\eta\to 0^+} &\left\{ \frac{\Omega_{t,ia}(\mathbf{k}) + U_{ia}^{(\mathscr{E}_t[\mp\omega])*}(\mathbf{k})B_{ia,ai}(\mathbf{k},\mathbf{k})}{\varepsilon_a^{(0)}(\mathbf{k}) - \varepsilon_i^{(0)}(\mathbf{k}) - B_{ia,ia}(\mathbf{k},\mathbf{k}) \pm \omega + \imath\eta} \right. \\ &\left. + \frac{\sum_{(\mathbf{k}',j,b)\neq(\mathbf{k},i,a)} \left(U_{jb}^{(\mathscr{E}_t[\pm\omega])}(\mathbf{k}')B_{ia,jb}(\mathbf{k},\mathbf{k}') + U_{jb}^{(\mathscr{E}_t[\mp\omega])*}(\mathbf{k}')B_{ia,bj}(\mathbf{k},\mathbf{k}')\right)}{\varepsilon_a^{(0)}(\mathbf{k}) - \varepsilon_i^{(0)}(\mathbf{k}) - B_{ia,ia}(\mathbf{k},\mathbf{k}) \pm \omega + \imath\eta} \right\} \end{aligned} \tag{44}$$

The dielectric matrix elements become infinite when $U_{ia}^{(\mathscr{E}_t[\pm\omega])}(\mathbf{k})$ is infinite, i.e. at each $i \to a$ resonance. According to the expression of the denominator in Eq. (44), the pole is shifted by the real $B_{ia,ia}(\mathbf{k},\mathbf{k})$ value with respect to the transition en-

[1] In going from Eq. (43) to Eq. (44), we use $x = \frac{a+bx}{c} \Rightarrow x(1-b/c) = \frac{a}{c}$ which leads to $x = \frac{a}{c-b}$

ergy $\varepsilon_a^{(0)}(\mathbf{k}) - \varepsilon_i^{(0)}(\mathbf{k})$ between unrelaxed crystalline orbitals, as in SOS, for each $\mathbf{k}$-point. This is the exciton effect for the monoexcitation $i_\mathbf{k} \rightarrow a_\mathbf{k}$, assuming there is no "overtone" due to other $j_{\mathbf{k}'} \rightarrow b_{\mathbf{k}'}$ resonances.
For computational purposes it is more convenient to obtain the transition frequencies directly using the standard TDHF format; in principle, the results are the same in either case. For this purpose we may start, again, with Eq. (40) but this time set η to zero and the perturbation $\Omega_{t,ia}(\mathbf{k}) = 0$. Note that the position of the poles is unaltered by the perturbation term. After multiplying both sides of Eq. (44) by the denominator $(\varepsilon_a^{(0)}(\mathbf{k}) - \varepsilon_i^{(0)}(\mathbf{k}) - B_{ia,ia}(\mathbf{k},\mathbf{k}) \pm \omega)$ and some mathematical manipulations, as well as use of the relation $U_{ia}^{(\mathscr{E}_t[\pm\omega])}(\mathbf{k}) = -U_{ai}^{(\mathscr{E}_t[\mp\omega])\,*}(\mathbf{k})$ (and $B_{ai,jb}(\mathbf{k},\mathbf{k}') = B^*_{ia,bj}(\mathbf{k},\mathbf{k}')$), we obtain the following pair of equations:

$$\begin{aligned}&(\varepsilon_i^{(0)}(\mathbf{k}) - \varepsilon_a^{(0)}(\mathbf{k}) + B_{ia,ia}(\mathbf{k},\mathbf{k}) - \omega)U_{ia}^{(\mathscr{E}_t[+\omega])}(\mathbf{k}) - B_{ia,ai}(\mathbf{k},\mathbf{k})U_{ai}^{(\mathscr{E}_t[+\omega])}(\mathbf{k}) \\ &+ \sum_{(\mathbf{k}',j,b)\neq(\mathbf{k},i,a)} \Big(B_{ia,jb}(\mathbf{k},\mathbf{k}')U_{jb}^{(\mathscr{E}_t[+\omega])}(\mathbf{k}') - B_{ia,bj}(\mathbf{k},\mathbf{k}')U_{bj}^{(\mathscr{E}_t[+\omega])}(\mathbf{k}')\Big) = 0\end{aligned} \tag{45}$$

and

$$\begin{aligned}&(\varepsilon_i^{(0)}(\mathbf{k}) - \varepsilon_a^{(0)}(\mathbf{k}) + B_{ai,ai}(\mathbf{k},\mathbf{k}) + \omega)U_{ai}^{(\mathscr{E}_t[+\omega])\,*}(\mathbf{k}) - B^*_{ai,ia}(\mathbf{k},\mathbf{k})U_{ia}^{(\mathscr{E}_t[+\omega])*}(\mathbf{k}) \\ &+ \sum_{(\mathbf{k}',j,b)\neq(\mathbf{k},i,a)} \Big(B^*_{ai,bj}(\mathbf{k},\mathbf{k}')U_{bj}^{(\mathscr{E}_t[+\omega])\,*}(\mathbf{k}') - B^*_{ai,jb}(\mathbf{k},\mathbf{k}')U_{jb}^{(\mathscr{E}_t[+\omega])\,*}(\mathbf{k}')\Big) = 0\end{aligned} \tag{46}$$

A pair of equations is obtained for each $jb,\mathbf{k}'$ transition giving rise to the well-known non-hermitian TDHF system of $2 \times N_{occ} \times N_{virt} \times N_\mathbf{k}$ equations for the eigenvectors $(X,Y) = (U_{ia,\mathbf{k}}^{(\mathscr{E}_t[\omega])}, U_{ai,\mathbf{k}}^{(\mathscr{E}_t[\omega])})$ (see also Refs. [27, 24]):

$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix} \tag{47}$$

where

$$A = \begin{pmatrix} \varepsilon_i^{(0)}(\mathbf{k}) - \varepsilon_a^{(0)}(\mathbf{k}) + B_{ia,ia}(\mathbf{k},\mathbf{k}) & B_{ia,jb}(\mathbf{k},\mathbf{k}') \\ B_{ia,jb}(\mathbf{k},\mathbf{k}') & \varepsilon_j^{(0)}(\mathbf{k}') - \varepsilon_b^{(0)}(\mathbf{k}') + B_{jb,jb}(\mathbf{k}',\mathbf{k}') \end{pmatrix} \tag{48}$$

and

$$B = \begin{pmatrix} -B_{ia,ai}(\mathbf{k},\mathbf{k}) & -B_{ia,bj}(\mathbf{k},\mathbf{k}') \\ -B_{ia,bj}(\mathbf{k},\mathbf{k}') & -B_{jb,bj}(\mathbf{k}',\mathbf{k}') \end{pmatrix} \tag{49}$$

The matrices in Eq. 47 have the dimension $2 \times N_{occ} \times N_{virt} \times N_\mathbf{k}$ on a side with N_{occ}, N_{virt} and $N_\mathbf{k}$ being, respectively, the number of occupied and virtual orbitals and the number of $\mathbf{k}$ points of the reciprocal space. Finally, the oscillator strengths are obtained from the eigenvectors and their transition moments.
Both methods of simulating the uv-visible absorption spectrum that were described here lead to the same results (poles and oscillator strengths) but via two different

approaches: either by diagonalization of the unperturbed hamiltonian in the $i_{\mathbf{k}} \rightarrow a_{\mathbf{k}}$ basis set or by plotting the imaginary part of the linear response to a dynamic field.

4.2 Dynamic First Hyperpolarizabilities

In order to derive our $2n+1$-rule working formula for the Hartree-Fock dynamic first hyperpolarizabilities of a 3D periodic system given by Eq. (50) below, we start with the expression for the static limit due to Ferrero, et al. [see Eq. (58) in Ref. [18]]. This expression has exactly the same form as that shown below except, of course, that all frequencies are set equal to zero. The 3D static result was obtained, in fact, by generalizing the 1D periodic frequency-dependent treatment of Kirtman et al. [30] which, in turn, was based on the time-dependent Hartree-Fock formulation for molecules developed by Karna and Dupuis [28] (KD). Thus, we use KD to introduce the 3D frequency-dependence.

KD considered just four special cases (see Table VII in Ref. [28]), including static, and their treatment pertains only to the first two terms in square brackets below. Nonetheless, it is straightforward to generalize their formulation as we have done. Finally, the use of the operator $P_{t[-\omega_\sigma]u[+\omega_1]v[+\omega_2]}$ which permutes the pairs $(t[-\omega_\sigma])$, $(u[+\omega_1])$, and $(v[+\omega_2])$ has been introduced by Orr and Ward [43], and used by Bishop and Kirtman in Ref. [5].

From the approach just described the general expression for the first hyperpolarizability of closed-shell periodic systems in the presence of frequency-dependent fields may be written as (see Ref. [53]):

$$\begin{aligned}
&\beta_{tuv}(-\omega_\sigma;\omega_1,\omega_2) = -\frac{\partial^3 E^{TOT}}{\partial \mathscr{E}_{t[-\omega_\sigma]} \partial \mathscr{E}_{u[\omega_1]} \partial \mathscr{E}_{v[\omega_2]}} \\
&= \frac{2}{n_k} \Re \left\{ P_{t[-\omega_\sigma],u[+\omega_1],v[+\omega_2]} \sum_{\mathbf{k}}^{BZ} Tr \left[n\, U^{(\mathscr{E}_{t[-\omega_\sigma]})^\dagger}(\mathbf{k}) \left(G^{(\mathscr{E}_{u[+\omega_1]})}(\mathbf{k}) U^{(\mathscr{E}_{v[+\omega_2]})}(\mathbf{k}) \right.\right.\right. \\
&\left.\left.\left. -U^{(\mathscr{E}_{v[+\omega_2]})}(\mathbf{k}) G^{(\mathscr{E}_{u[+\omega_1]})}(\mathbf{k}) + \imath \frac{\partial U^{(\mathscr{E}_{v[+\omega_2]})}(\mathbf{k})}{\partial k_u} \right) \right] \right\}
\end{aligned} \tag{50}$$

where $\omega_\sigma = \omega_1 + \omega_2$. The last term of Eq. 50 appears only for infinite periodic systems. A working expression is:

$$\frac{\partial U_{ia}^{(\mathscr{E}_{v[+\omega_2]})}(\mathbf{k})}{\partial k_u} = \frac{\frac{\partial}{\partial k_u} G_{ia}^{(\mathscr{E}_{v[+\omega_2]})}(\mathbf{k})}{\varepsilon_a^{(0)}(\mathbf{k}) - \varepsilon_i^{(0)}(\mathbf{k}) + \omega_2} - \frac{G_{ia}^{(\mathscr{E}_{v[+\omega_2]})}(\mathbf{k}) \frac{\partial}{\partial k_u} \left(\varepsilon_a^{(0)}(\mathbf{k}) - \varepsilon_i^{(0)}(\mathbf{k}) \right)}{\left(\varepsilon_a^{(0)}(\mathbf{k}) - \varepsilon_i^{(0)}(\mathbf{k}) + \omega_2 \right)^2} \tag{51}$$

in which the development of $\frac{\partial}{\partial k_u} G_{ia}^{(\mathscr{E}_{v[+\omega_2]})}(\mathbf{k})$, the second derivative of the Fock matrix elements $F_{ia}(\mathbf{k})$ with respect to the field and $\mathbf{k}$, can be found in Ref. [30]:

$$\begin{aligned} \frac{\partial G_{ia}^{(\mathscr{E}_{v[+\omega_2]})}(\mathbf{k})}{\partial k_u} = & \sum_p^{all} \left(Q_{pi}^u(\mathbf{k}) \right)^* G_{pa}^{(\mathscr{E}_{v[+\omega_2]})}(\mathbf{k}) + \sum_p^{all} G_{ip}^{(\mathscr{E}_{v[+\omega_2]})}(\mathbf{k}) Q_{pa}^u(\mathbf{k}) \\ & + \sum_{\mu,\nu} C_{\mu i}^{(0)*}(\mathbf{k}) \frac{\partial F_{\mu\nu}^{(\mathscr{E}_{v[+\omega_2]})}(\mathbf{k})}{\partial k_u} C_{\nu a}^{(0)}(\mathbf{k}) \end{aligned} \tag{52}$$

The evaluation of the last term on the r.h.s. of Eq. (52) is straightforward except for the term $\frac{\partial Q_{pq}^v}{\partial k_u}$ contained in it. This term, however, does not depend on the ω_2 frequency, and can be thus computed as in the static case [4, 18]. As regards the calculation of $\frac{\partial \varepsilon_i^{(0)}}{\partial k_u}$ it is equal to: $\sum_{\mu,\nu} C_{\mu i}^{(0)*}(\mathbf{k}) \left(\frac{\partial F_{\mu\nu}^{(0)}}{\partial k_u} - \varepsilon_i^{(0)} \frac{\partial S_{\mu\nu}}{\partial k_u} \right) C_{\nu i}^{(0)}(\mathbf{k})$. As in the case of the static first hyperpolarizability there is an additional XC contribution in DFT to the corresponding dynamic property. Within the adiabatic approximation the generalization to frequency-dependent fields is [37]:

$$\begin{aligned} \beta_{tuv}^{DFT}(-\omega_\sigma;\omega_1,\omega_2) = \sum_i w_i P_{t[-\omega_\sigma],u[+\omega_1],v[+\omega_2]} \Bigg[& \frac{\partial^3 f^{XC}}{\partial \rho^3} \rho_{(-\omega_\sigma)}^t \rho_{(+\omega_1)}^u \rho_{(+\omega_2)}^v \\ & + 2 \frac{\partial^3 f^{XC}}{\partial \rho^2 \partial \mid \nabla\rho \mid^2} \left(\rho_{(-\omega_\sigma)}^t \rho_{(+\omega_1)}^u \nabla\rho \cdot \nabla\rho_{(+\omega_2)}^v \right) \\ & + 4 \frac{\partial^3 f^{XC}}{\partial \rho \partial (\mid \nabla\rho \mid^2)^2} \left(\rho_{(-\omega_\sigma)}^t \nabla\rho \cdot \nabla\rho_{(+\omega_1)}^u \nabla\rho \cdot \nabla\rho_{(+\omega_2)}^v \right) \\ & + 8 \frac{\partial^3 f^{XC}}{\partial (\mid \nabla\rho \mid^2)^3} \nabla\rho \cdot \nabla\rho_{(-\omega_\sigma)}^t \nabla\rho \cdot \nabla\rho_{(+\omega_1)}^u \nabla\rho \cdot \nabla\rho_{(+\omega_2)}^v \\ & + 2 \frac{\partial^2 f^{XC}}{\partial \rho \partial \mid \nabla\rho \mid^2} \left(\rho_{(-\omega_\sigma)}^t \nabla\rho_{(+\omega_1)}^u \cdot \nabla\rho_{(+\omega_2)}^v \right) \\ & + 4 \frac{\partial^2 f^{XC}}{(\partial (\mid \nabla\rho \mid^2)^2} \left(\nabla\rho \cdot \nabla\rho_{(-\omega_\sigma)}^t \nabla\rho_{(+\omega_1)}^u \cdot \nabla\rho_{(+\omega_2)}^v \right) \Bigg]_{\mathbf{r_i}} \end{aligned} \tag{53}$$

in which the frequency-dependent density and density gradient are:

$$\rho^t_{(\pm\omega)}(r_i) = \sum_{\mu,\nu}\sum_g D_{\mu\nu}^{(\mathscr{E}_{t[\pm\omega]})}(\mathbf{g})\,\chi^0_\mu(r_i)\chi^g_\nu(r_i) \tag{54}$$

and

$$\nabla\rho^t_{(\pm\omega)}(r_i) = \sum_{\mu,\nu}\sum_g D_{\mu\nu}^{(\mathscr{E}_{t[\pm\omega]})}(\mathbf{g})\,\nabla(\chi^0_\mu(r)\chi^g_\nu(r))_{r_i} \tag{55}$$

In principle, exactly the same approach as applied here to obtain the dynamic first hyperpolarizability can be employed for the dynamic second hyperpolarizability. That is a project, however, which remains to be done. When completed it will provide access to properties such two-photon absorption, field-induced second harmonic generation and the optical Kerr effect among others.

5 Effects of geometric distortions on cell dipole and polarizability

In this section, we will discuss how the coupled-perturbed methods presented in previous sections can be combined with analytical gradients - with respect to either atomic positions or cell shape - to yield mixed derivatives. Some of the most interesting experimentally observable quantities arising from such treatment are:

$$\text{Infrared Intensities (Born charges)} \Longleftarrow \frac{\partial}{\partial \mathscr{E}_t} \frac{\partial E^{TOT}}{\partial \mathscr{R}_v^A}\bigg|_{\mathscr{E}=0,\mathscr{R}_0} \tag{56}$$

$$\text{Raman Intensities} \Longleftarrow \frac{\partial^2}{\partial \mathscr{E}_t \partial \mathscr{E}_u} \frac{\partial E^{TOT}}{\partial \mathscr{R}_v^A}\bigg|_{\mathscr{E}=0,\mathscr{R}_0} \tag{57}$$

$$\text{Piezoelectric tensor} \Longleftarrow \frac{\partial}{\partial \mathscr{E}_t} \frac{\partial E^{TOT}}{\partial a_{\alpha v}}\bigg|_{\mathscr{E}=0,a^0} \tag{58}$$

$$\text{Photoelastic Tensor} \Longleftarrow \frac{\partial^2}{\partial \mathscr{E}_t \mathscr{E}_u} \frac{\partial E^{TOT}}{\partial a_{\alpha v}}\bigg|_{\mathscr{E}=0,a^0} \tag{59}$$

$$\tag{60}$$

Here, as in previous sections, t,u,v are cartesian directions, $\mathscr{R}_v^A$ represents a displacement of atom A along cartesian direction v, and $\mathscr{R}_0$ represents the equilibrium (optimized) geometry of the atoms within the unit cell. Analogously, $a_{\alpha v}$ are Cartesian components of the three (in the 3D case) lattice vectors $\mathbf{a}_\alpha$, $\alpha = 1,2,3$ and a^0 represents the equilibrium (optimized) set of lattice parameters.

When such mixed derivatives are considered, the 2n+1 rule breaks down. In the case of Raman intensities, for example, third-order energy derivatives are needed and second-order wavefunction derivatives are required. But there is a choice. One may determine either mixed second derivatives or second-order electric field derivatives. The latter is preferred since the calculations scale more favorably with respect to the size of the unit cell due to the smaller number of perturbation equations to be solved. Details of the derivation of optimal and computable expressions for Equations (56), (57) and (58) above can be found in Refs. [35, 34], [36] and [1], while work for analytical implementation of photoelasticity is in progress.

Unlike the pure electric field case treated in previous sections, we now have to consider gradients of mono- and bi-electronic integrals over atomic orbitals, since now they depend on the perturbation. However, the time-consuming calculation of derivatives of orbital coefficients with respect to nuclear displacements is avoided by taking advantage of the eigenvalue-weighted density matrix. Finally, derivatives with respect to the wave-vector are carried out analytically, so that the entire treatment is analytical. In the following, we briefly review the operative equations, underlining their key aspects in connection with the discussion in previous sections.

5.1 Infrared and Raman intensities

The mixed second derivatives of the total energy with respect to the atomic displacements and the electric field (along b), which determine the infrared transition intensities, are conveniently formulated in direct space as:

$$\begin{aligned}
&\frac{\partial}{\partial \mathscr{E}_t}\frac{\partial E^{TOT}}{\partial \mathscr{R}_v^A}\bigg|_{\mathscr{E}=0,\mathscr{R}_0} \\
&= \mathrm{Tr}\left(\frac{1}{2}\left(H^{(\mathscr{R}_v^A)}(\mathbf{g})+\mathfrak{F}^{(\mathscr{R}_v^A)}(\mathbf{g})\right)^{(0)} D^{(\mathscr{E}_t)}(\mathbf{g})\right. \\
&+\frac{1}{2}\left[\Omega_t^{(\mathscr{R}_v^A)}(\mathbf{g})+\left(\mathfrak{F}^{(\mathscr{R}_v^A)}(\mathbf{g})\right)^{(\mathscr{E}_t)}\right] D^{(0)}(\mathbf{g}) - S^{(\mathscr{R}_v^A)}(\mathbf{g})\, D_W^{(\mathscr{E}_t)}(\mathbf{g})\Bigg)_{\mathscr{R}_0} \\
&-Z_A\delta_{tv} \quad ,
\end{aligned} \tag{61}$$

These derivatives are evaluated at zero field and equilibrium geometry. In Eq. (61) Z_A is the nuclear charge of atom A and $H(\mathbf{g})$ is the core Hamiltonian. The notation $\mathfrak{F}^{(\mathscr{R}_v^A)}$ signifies that the derivative of the Fock matrix $F(\mathbf{g})$ is taken with respect to atomic displacements while holding the density matrix constant. Note that the definition of the "eigenvalue-weighted density matrix" $D_W(\mathbf{g})$ given by

$$D_W(\mathbf{g}) = \sum_{\mathbf{k}}^{BZ} C(\mathbf{k})\varepsilon(\mathbf{k})C^{\dagger}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{g}} \tag{62}$$

allows the computation of its perturbed form $D_W^{(\mathscr{E}_t)}(\mathbf{g})$ as:

$$D_W^{(\mathscr{E}_t)}(\mathbf{g}) = \sum_{\mathbf{k}}^{BZ}\left(C^{(\mathscr{E}_t)}(\mathbf{k})\varepsilon(\mathbf{k})C^{\dagger}(\mathbf{k}) + C(\mathbf{k})\varepsilon^{(\mathscr{E}_t)}(\mathbf{k})C^{\dagger}(\mathbf{k}) + C(\mathbf{k})\varepsilon(\mathbf{k})C^{(\mathscr{E}_t)\,\dagger}(\mathbf{k})\right)e^{i\mathbf{k}\cdot\mathbf{g}} \tag{63}$$

As widely discussed in previous sections, the $Q(\mathbf{k})$ matrix [Eq. (26)] contains undetermined imaginary diagonal elements that could, in principle, pose problems in solving equation 61. However, the derivative of these matrix elements with respect to the atomic displacements of interest vanishes because the derivatives are taken with the unit cell parameters held fixed. Thus, the dependence on the crystal boundaries vanishes and the physical quantity is correctly obtained.

The Raman intensities involve one further derivative with respect to the electric field and we obtain the following expression for the Raman tensor in Cartesian coordinates [36]:

$$\frac{\partial^2}{\partial\mathscr{E}_t\partial\mathscr{E}_u}\frac{\partial E^{TOT}}{\partial\mathscr{R}_v^A}\bigg|_{\mathscr{E}=0,\mathscr{R}_0} = \mathrm{Tr}\Bigg\{\frac{1}{2}\left(H^{(\mathscr{R}_v^A)}(\mathbf{g})+\mathfrak{F}^{(\mathscr{R}_v^A)}(\mathbf{g})\right)^{(0)}D^{(\mathscr{E}_t,\mathscr{E}_u)}(\mathbf{g}) + \frac{1}{2}P_{t,u}\left[\left(\Omega_t^{(\mathscr{R}_v^A)}(\mathbf{g})+\left(\mathfrak{F}^{(\mathscr{R}_v^A)}(\mathbf{g})\right)^{(\mathscr{E}_t)}\right)D^{(\mathscr{E}_u)}(\mathbf{g})\right] + \frac{1}{2}\left[P_{t,u}\,\Omega_t^{(\mathscr{R}_v^A,\mathscr{E}_u)}+\left(\mathfrak{F}^{(\mathscr{R}_v^A)}(\mathbf{g})\right)^{(\mathscr{E}_t,\mathscr{E}_u)}\right]D^{(0)}(\mathbf{g}) - S^{(\mathscr{R}_v^A)}(\mathbf{g})\,D_W^{(\mathscr{E}_t,\mathscr{E}_u)}(\mathbf{g})\Bigg\}_{\mathscr{R}_0} \tag{64}$$

In Eq. (66) all quantities have been defined in connection to Eq. (61). $D_W^{(\mathscr{E}_t,\mathscr{E}_u)}(\mathbf{g})$, in particular, is obtained by differentiating Eq. (63) with respect to a second field $\mathscr{E}_u$). The notation $\left(\mathfrak{F}^{(\mathscr{R}_v^A)}(\mathbf{g})\right)^{(\mathscr{E}_t)}$ signifies that perturbation in the Fock matrix with respect to atomic displacements is taken at constant density, but perturbation with respect to the electric field affects the density. As in the case of infrared intensities, it can be shown [36] that the diagonal elements of $Q(\mathbf{k})$ vanish when the above expression is evaluated. This must be true since these elements do not contribute to the polarizability.

We remark that in equations (61) and (64) - as well as in (72) below - all ingredients are obtained either by a coupled-perturbed self-consistent procedure or through analytical gradients of the AO integrals. Although not immediately obvious, no mixed derivatives of any matrix appear and there are no derivatives of the density matrix (or eigenvalue-weighted density matrix) with respect to atomic displacements.

5.2 The Piezoelectric tensor

The "proper" direct piezoelectric response of a crystal is represented by a third-rank tensor that is the sum of an electronic and a nuclear term, $\mathbf{e} = \mathbf{e}^{\mathrm{ele}} + \mathbf{e}^{\mathrm{nuc}}$.[1] The electronic term measures the variation of the current density J with strain when no nuclear relaxation is allowed (clamped-nuclei condition, *clamp*) [64]:

$$e_{tuv}^{\mathrm{ele}} = \frac{\partial J_t}{\partial\varepsilon_{uv}}\bigg|_{clamp} = \sum_\alpha \frac{\partial J_t}{\partial a_{\alpha u}}a_{\alpha v}\bigg|_{clamp}. \tag{65}$$

Here ε is the symmetric second-rank pure strain tensor and the $a_{\alpha v}$ are Cartesian components of the three lattice vectors $\mathbf{a}_\alpha$, $\alpha = 1,2,3$. The nuclear relaxation contribution can be expressed as [57]:

$$e_{tuv}^{\mathrm{nuc}} = \frac{1}{V}\sum_s \frac{\partial^2 E^{TOT}}{\partial\mathscr{E}_t\partial u_s}\frac{\mathrm{d}u_s}{\mathrm{d}\varepsilon_{uv}}, \tag{66}$$

where $V = \mathbf{a}_1\cdot(\mathbf{a}_2\times\mathbf{a}_3)$ is the cell volume and the u_s are $3N-3$ fractional coordinates (N being the number of atoms per cell) obtained from the $3N$ atomic fractional

coordinates by orthogonalization to the three translations along $\hat{x}$, $\hat{y}$ and $\hat{z}$.
The $\mathrm{d}u_s/\mathrm{d}\varepsilon_{jk}$ derivatives can be obtained in either of two ways: i) optimization of the internal geometry at strained configurations or ii) from the full Hessian matrix **H** of energy second derivatives with respect to both fractional atomic displacements and lattice deformations (with a truncation to quadratic terms in the Taylor's expansion of the energy) [65]. We have found that ii) is preferable [1]. In that procedure the following relation is utilized:

$$\frac{\mathrm{d}u_s}{\mathrm{d}\varepsilon_{jk}} = -\sum_{s'=1}^{3N-3} H_{jk,s'} \times (H^{-1})_{s's} \;, \tag{67}$$

in which

$$H_{jk,s'} = \left(\frac{\partial^2 E}{\partial \varepsilon_{jk} \partial u_{s'}} \right) \;, \tag{68}$$

and $(H^{-1})_{s's}$ is an element of the inverse of the atomic Hessian:

$$H_{s's} = \left(\frac{\partial^2 E}{\partial u_{s'} \partial u_s} \right) \;. \tag{69}$$

We can now write the electronic contribution to the "proper" piezoelectric tensor in terms of the polarization **P** as [64]:

$$e^{\mathrm{ele}}_{tuv} = \left.\frac{\partial J_t}{\partial \varepsilon_{uv}}\right|_{clamp} = \left.\frac{\partial P_t}{\partial \varepsilon_{uv}}\right|_{clamp} + P_t \delta_{uv} - P_v \delta_{tu} \;, \tag{70}$$

with the first term on the right-hand-side being the electronic contribution to the "improper" piezoelectric tensor. By expressing the polarization in terms of a total energy derivative, and by exploiting the second equality in equation (65), one gets:

$$\left.\frac{\partial J_t}{\partial \varepsilon_{uv}}\right|_{clamp} = \frac{1}{V} \sum_{\alpha} a_{\alpha v} \left.\frac{\partial^2 E^{TOT}}{\partial \mathscr{E}_t \partial a_{\alpha u}}\right|_{clamp} - P_v \delta_{tu} \;. \tag{71}$$

The analogue of Equation (61), where the nuclear displacements are replaced by cell deformations, can be cast (for equilibrium lattice parameters a^0) as:

$$\begin{aligned} \frac{\partial}{\partial \mathscr{E}_t} \left.\frac{\partial E^{TOT}}{\partial a_{\alpha v}}\right|_{\mathscr{E}=0,a^0} = \mathrm{Tr} \Bigg(& \left[H^{(a_{\alpha v})}(\mathbf{g}) + \mathfrak{F}^{(a_{\alpha v})}(\mathbf{g}) \right] D^{(\mathscr{E}_t)}(\mathbf{g}) \\ & + \frac{1}{2} \left[\Omega_t^{(a_{\alpha v})}(\mathbf{g}) + \left(\mathfrak{F}^{(a_{\alpha v})}(\mathbf{g}) \right)^{(\mathscr{E}_t)} \right] D^{(0)}(\mathbf{g}) - S^{(a_{\alpha v})}(\mathbf{g}) D_W^{(\mathscr{E}_t)}(\mathbf{g}) \Bigg)_{a^0} \\ & - \sum_A Z_A f_{A,\alpha} \delta_{tv} + e \delta_{tv} N_\alpha \;, \end{aligned} \tag{72}$$

where $D_W^{(\mathscr{E}_t)}(\mathbf{g})$ is defined in Eq. (63). $f_{A,\alpha}$ is the fractional coordinate of atom A along lattice vector α, that is $\mathscr{R}_t^A = \sum_\alpha f_{A,\alpha} a_{\alpha t}$, e is the magnitude of the electron charge and N_α is an arbitrary integer, arising from the imaginary diagonal elements of $Q(\mathbf{k})$. While the latter term appears for the improper piezoelectricity [30] , it vanishes for the "proper" one since it is exactly cancelled by the $-P_v\delta_{tu}$ term in Eq. (71).

5.3 Extension to DFT

The extension of the above expressions for the infrared, Raman and piezoelectric tensors to DFT is done along the same lines as for the polarizability and hyperpolarizability discussed in Section 3.2. We report here, as a representative case, the expression for the closed-shell Born charges (infrared) tensor:

$$\begin{aligned}
&\left.\frac{\partial E_R^{XC(\mathscr{R}_v^A)}}{\partial \mathscr{E}_t}\right|_{\mathscr{E}=0,\mathscr{R}_0} \\
&= \sum_i w_i \left\{ \left[\frac{\partial^2 f^{XC}}{\partial \rho^2} \frac{\partial \rho}{\partial \mathscr{E}_t} + \frac{\partial^2 f^{XC}}{\partial \rho\, \partial |\nabla\rho|^2} \frac{\partial |\nabla\rho|^2}{\partial \mathscr{E}_t} \right] \rho^{(\mathscr{R}_v^A)} \right. \\
&+ 2 \left[\frac{\partial^2 f^{XC}}{\partial (|\nabla\rho|^2)^2} \frac{\partial |\nabla\rho|^2}{\partial \mathscr{E}_t} \nabla\rho + \frac{\partial^2 f^{XC}}{\partial \rho\, \partial |\nabla\rho|^2} \frac{\partial \rho}{\partial \mathscr{E}_t} \nabla\rho + \frac{\partial f^{XC}}{\partial |\nabla\rho|^2} \frac{\partial \nabla\rho}{\partial \mathscr{E}_t} \right] \cdot \nabla\rho^{(\mathscr{R}_v^A)} \\
&+ \left. \frac{\partial f^{XC}}{\partial \rho} \frac{\partial \rho^{(\mathscr{R}_v^A)}}{\partial \mathscr{E}_t} + 2 \frac{\partial f^{XC}}{\partial |\nabla\rho|^2} \nabla\rho \cdot \frac{\partial \nabla\rho^{(\mathscr{R}_v^A)}}{\partial \mathscr{E}_t} \right\}_{\mathbf{r}_i} \\
&+ \sum_i \frac{\partial w_i}{\partial \mathscr{R}_v^A} \left\{ \frac{\partial f^{XC}}{\partial \rho} \frac{\partial \rho}{\partial \mathscr{E}_t} + \frac{\partial f^{XC}}{\partial |\nabla\rho|^2} \frac{\partial |\nabla\rho|^2}{\partial \mathscr{E}_t} \right\}_{\mathbf{r}_i}
\end{aligned} \tag{73}$$

There are two key differences due to replacing an electric field derivative by a derivative with respect to an atomic displacement. One is that the AO derivatives in the expression for the density no longer vanish. The other is that the dependence of the weights on the atomic position must be taken into account as in the last term of Eq. (73).

5.4 Converse piezoelectric effect

Piezoelectricity is a coupling between electrical and mechanical responses of a system. Whereas the piezoelectric effect describes the generation of polarization due to mechanical strain or stress, the converse piezoelectric effect describes the generation of strain or stress due to an applied electric field or voltage. Thus, in both cases structural as well as electronic responses are at the center of attention.

When structural responses to an electric field are accounted for some subtleties occur. The responses in the bulk of any large, finite sample (modeled as being infinite and periodic) may contain a finite contribution from the boundaries of the sample irrespective of its size as long as the sample is so large that the thermodynamic limit has been reached. Therefore, different piezoelectric property values may be obtained for samples of the same material that differ only in shape and/or surface charges. In addition, as a secondary effect, differences in the piezoelectric structural response, may also lead to differences in other properties.

Mathematically, when the system is described as being infinite and periodic, the information on the effects due to the shape and/or surface charges are contained in (**k** and band dependent) crystal orbital phase factors. Thus, even if the effects are due to the boundaries of the sample, they can, in principle, be calculated as a bulk property in the sense that the effects are contained in the information for the infinite, periodic system.

It is easy to verify that the crystal orbital phase factors show up in the imaginary part of the diagonal elements of the Q matrices. As long as it can be assumed that the applied electric field does not change the lattice vectors, the imaginary parts of the diagonal elements of the Q matrices can be ignored. This is the case for high frequency fields. However, for the converse piezoelectric effect the applied electric field has an essentially vanishing frequency and the changes in the lattice vectors due to the applied field are the quantities of interest.

If a_{ij} is the j-th component of the i-th lattice vector and F_k is the kth component of the vector describing the field (see further below), a converse piezoelectric tensor may be defined as

$$\eta_{ijk} = \left.\frac{\partial a_{ij}}{\partial F_k}\right|_{F_k=0} . \tag{74}$$

When $\mathbf{F} = \mathscr{E}$, it can be shown [39] that one may write

$$\eta_{ijk} = \eta_{ijk,0} + \tilde{n}_{ijk}\eta_{ijk,1}, \tag{75}$$

where $\eta_{ijk,0}$ is a reference value and different values of $\tilde{n}_{ijk}$ correspond to modeling samples of different shapes and/or surface charges. For chemical/physical reasons, $\tilde{n}_{ijk}$ cannot vary more than roughly $-2 \leq \tilde{n}_{ijk} \leq +2$.

At this time we do not know the precise relation between the parameters $\tilde{n}_{ijk}$ and the shape/surface charge of a given sample, which implies that when calculating the converse piezoelectric tensor, deviations between theory and experiment may be due either to theoretical and experimental inaccuracies or to differences in the shape/surface charges. A relevant question, therefore, is whether $\eta_{ijk,1}/\eta_{ijk,0}$ is so small that $\eta_{ijk,1}$ can be ignored. Exploratory calculations on some perovskite crystals [39] have shown that $\eta_{ijk,1}/\eta_{ijk,0}$ is typically about 1/10, but larger (and smaller) values can be obtained.

A special case is that of quasi-one-dimensional systems (chains). For the components parallel to the chain direction (defined as z), $\tilde{n}_{zzz}$ can take only integral values.

Moreover, if $\mathbf{F}$ is taken to be the potential drop over one unit cell (i.e., $F_z = \mathscr{E}_z a_{zz}$), then η_{zzz} becomes independent of $\tilde{n}_{zzz}$.

6 Summary and Prospects

Our overall goal has been to put property calculations for infinite periodic systems on the same footing as the corresponding calculations for ordinary molecules. The CRYSTAL computer program is well-suited for this task since it utilizes Gaussian-type basis functions and takes maximum advantage of symmetry. Considerable progress has been made in adapting the treatment of molecules to account for the change in boundary conditions and subsequently implementing the appropriate methodology in CRYSTAL. This is particularly so for electric field properties as well as mixed properties involving a combination of electric fields and geometric displacements. For the former, we have adopted the coupled perturbed Hartree-Fock and Kohn-Sham (CPHF/CPKS) approaches to treat linear polarizabilities and nonlinear optical properties. Although the most important second-order nonlinear optical properties, including second harmonic generation and the dc-Pockels effect, are now available the treatment of arbitrary frequencies and third-order properties remains to be accomplished in the near term. We have now also implemented the determination of optical spectra through the frequency-dependent linear polarizability. As far as the mixed derivatives are concerned, infrared and Raman spectra have been completed as well as the piezoelectric effect. Immediate next steps in this category include the hyper-Raman effect and photoelasticity.

Our treatment of the orbital electronic response to a magnetic field is still in its early stages. A new translationally invariant form for the interaction Hamiltonian, which allows for a simultaneous electric field so as to treat chiral properties, has been presented. However, the CPHF/CPKS perturbation treatment remains to be formulated and implemented.

The P (Parallel) and MPP (Massive Parallel Processing) versions of the code for the electric field properties is at an advanced stage. Right now it is possible to compute frequencies and IR intensities of systems up to about 1000 atoms in the unit cell; Raman intensities, first and second hyperpolarizabilities will become feasible for systems of this size in the near future.

Vibrational contributions to nonlinear optical properties can also be evaluated, but only in the static or high frequency limit and only in the lowest order of approximation (known as the finite field nuclear relaxation (FF-NR) treatment). FF-NR requires a geometry optimization in the presence of a finite field. At present the finite field can be applied only in a non-periodic, direction for 1D or 2D systems. This limits the tensor components that can be considered. Removal of these several restrictions can be envisioned, but certainly that will be a longer term effort.

Another longer-term perspective is the development of optical properties calculations for solids at the post-Hartree-Fock level. This could be done in connection with the local-correlation CRYSCOR code, [47, 48, 49] which presently features a very efficient implementation of the local MP2 approach for periodic systems. This implementation makes use of advanced techniques such as density fitting [38] and orbital-specific virtuals [62], as well as efficient parallel implementation.[33] The extension to local coupled-cluster is also envisaged in the future.

The treatment of properties associated with the orbital electronic response to a mag-

netic field is still in its infancy. A new periodic formulation of the interaction Hamiltonian has been presented. However, the CPHF/CPKS An appropriate Hamiltonian for the response to a homogeneous static field was presented in Sec.3. There already exist methods for the computation of magnetic shielding and magnetic susceptibilities, but this Hamiltonian opens the possibility for a new approach to these properties. Further down the line, in combination with electric fields, we should be able to obtain various optical rotatory properties, such as circular dichroism and Faraday rotation. At the moment, however, it remains to develop the CPHF/CPKS formulation along with the response to frequency-dependent magnetic fields.

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